

FORM PTO-1390 (Modified) (REV 11-2000)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER <b>30394-1045</b>	
<b>TRANSMITTAL LETTER TO THE UNITED STATES</b> <b>DESIGNATED/ELECTED OFFICE (DO/EO/US)</b> <b>CONCERNING A FILING UNDER 35 U.S.C. 371</b>				U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5) <div style="font-size: 1.5em; font-weight: bold; text-align: center;">09/857006</div>	
INTERNATIONAL APPLICATION NO. <b>PCT/NL00/00740</b>		INTERNATIONAL FILING DATE <b>16 October 2000</b>		PRIORITY DATE CLAIMED <b>15 October 1999</b>	
TITLE OF INVENTION <b>Process for the Preparation of Anionic Aqueous Polymer dispersions Containing No Volatile Tertiary Amine, Obtained Dispersion and Coating Resulting From Said Dispersion</b>					
APPLICANT(S) FOR DO/EO/US <b>Josep OLLER CHIRIVELLA Mario JIMENEZ MARTINEZ and Montserrat POUS BRUTAU</b>					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:					
<ol style="list-style-type: none"> <li>1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li>2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li>3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.</li> <li>4. <input type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31).</li> <li>5. <input type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371 (c) (2))           <ol style="list-style-type: none"> <li>a. <input type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau).</li> <li>b. <input type="checkbox"/> has been communicated by the International Bureau.</li> <li>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</li> </ol> </li> <li>6. <input type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).           <ol style="list-style-type: none"> <li>a. <input type="checkbox"/> is attached hereto.</li> <li>b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4).</li> </ol> </li> <li>7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))           <ol style="list-style-type: none"> <li>a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau).</li> <li>b. <input type="checkbox"/> have been communicated by the International Bureau.</li> <li>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</li> <li>d. <input type="checkbox"/> have not been made and will not be made.</li> </ol> </li> <li>8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</li> <li>9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).</li> <li>10. <input type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).</li> <li>11. <input type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409).</li> <li>12. <input checked="" type="checkbox"/> A copy of the International Search Report (PCT/ISA/210).</li> </ol> <p><b>Items 13 to 20 below concern document(s) or information included:</b></p> <ol style="list-style-type: none"> <li>13. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</li> <li>14. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</li> <li>15. <input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment.</li> <li>16. <input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment.</li> <li>17. <input type="checkbox"/> A substitute specification.</li> <li>18. <input type="checkbox"/> A change of power of attorney and/or address letter.</li> <li>19. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.</li> <li>20. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4).</li> <li>21. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).</li> <li>22. <input checked="" type="checkbox"/> Certificate of Mailing by Express Mail</li> <li>23. <input checked="" type="checkbox"/> Other items or information:</li> </ol> <p><b>Unsigned Declaration and Power of Attorney for Patent Application</b>  <b>Associate Power of Attorney</b></p> <p><b>THIS IS A NATIONAL ENTRY APPLICATION UNDER CHAPTER I, HAVING DESIGNATED THE U.S.</b></p>					

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5) <b>09/857006</b>		INTERNATIONAL APPLICATION NO. <b>PCT/NL00/00740</b>		ATTORNEY'S DOCKET NUMBER <b>30394-1045</b>	
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24. The following fees are submitted:

BASIC NATIONAL FEE ( 37 CFR 1.492 (a) (1) - (5) ) :				CALCULATIONS PTO USE ONLY	
<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO .....	\$1000.00				
<input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO .....	\$860.00				
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO .....	\$710.00				
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) .....	\$690.00				
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) .....	\$100.00				
<b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				<b>\$860.00</b>	
Surcharge of <b>\$130.00</b> for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).				<b>\$0.00</b>	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	16 - 20 =	0	x \$18.00	<b>\$0.00</b>	
Independent claims	1 - 3 =	0	x \$80.00	<b>\$0.00</b>	
Multiple Dependent Claims (check if applicable). <input type="checkbox"/>				<b>\$0.00</b>	
<b>TOTAL OF ABOVE CALCULATIONS =</b>				<b>\$860.00</b>	
<input type="checkbox"/> Applicant claims small entity status. (See 37 CFR 1.27). The fees indicated above are reduced by 1/2.				<b>\$0.00</b>	
<b>SUBTOTAL =</b>				<b>\$860.00</b>	
Processing fee of <b>\$130.00</b> for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).				<b>\$0.00</b>	
<b>TOTAL NATIONAL FEE =</b>				<b>\$860.00</b>	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). <input type="checkbox"/>				<b>\$0.00</b>	
<b>TOTAL FEES ENCLOSED =</b>				<b>\$860.00</b>	
				Amount to be: refunded	\$
				charged	\$

a. ☒ A check in the amount of **\$860.00** to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \_\_\_\_\_ to cover the above fees. A duplicate copy of this sheet is enclosed.


c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. **13-4213** A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.

**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

CUSTOMER NO. 005179



**05179**

PATENT TRADEMARK OFFICE

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SIGNATURE \_\_\_\_\_

**Jeffrey D. Myers**

NAME \_\_\_\_\_

**35,964**

REGISTRATION NUMBER \_\_\_\_\_

**29 May 2001**

DATE \_\_\_\_\_

I hereby certify that this paper is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 via EL762005695US on 29 May 2001, addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.

*Annette M. Turk*  
Annette M. Turk, Legal Assistant

29 May 2001  
Date Signed

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Josep OLLER CHIRIVELLA,  
Mario JIMÉNEZ MARTINEZ and Montserrat POUS BRUTAU

Serial No.: UNKNOWN

Filed: HEREWITH (29 May 2001)

For: PROCESS FOR THE PREPARATION OF ANIONIC  
AQUEOUS POLYMER DISPERSIONS CONTAINING NO  
VOLATILE TERTIARY AMINE, OBTAINED DISPERSION  
AND COATING RESULTING FROM SAID DISPERSION

PRELIMINARY AMENDMENT

Box: PCT  
Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

Please amend the application, without prejudice, as follows:

In the Claims:

Amend the claims as follows:

1. (Amended) A process for the preparation of an aqueous dispersion of an anionic polyurethane in which initially a tertiary aminofunctional acrylic monomer of formula I:



wherein

$\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  are organic groups which have no reactivity towards the double bond or the tertiary amine function,

is used as neutralizing agent for pendant carboxylic acid groups in dispersions of a polyurethane or a polyurethane-polyacrylate, whereafter the unsaturated monomers undergo in situ an addition polymerization,

wherein the aqueous dispersion of the anionic polyurethane is prepared by the steps of preparing an isocyanate functional anionic polyurethane prepolymer, optionally in the presence of vinylic monomers mixing the isocyanate terminated anionic polyurethane prepolymer with a tertiary-amino functional unsaturated monomer and optionally other vinylic monomers followed by dispersing of the obtained mixture into water, and chain extension of the polyurethane prepolymer with an active hydrogen compound during or after the dispersion in water, initiating radical polymerization of the vinylic monomers, including the tertiary amino functional unsaturated monomers.

2. (Amended) A process according to claim 1, in which the isocyanate terminated prepolymer is reacted with 0-100% of a stoichiometric amount of a hydroxy functional unsaturated monomer before the dispersion of water.

3. (Amended) A process according to claim 1, in which the tertiary amine functional acrylic oligomer or polymer is formed during the process by radical polymerization of tertiary amine functional unsaturated monomers.

4. (Amended) A process according to claim 1, in which the tertiary amine functional unsaturated monomers react together with other vinylic monomers during the radical polymerization to obtain a tertiary amine functional co-polymer.

5. (Amended) A process according to claim 1, wherein the tertiary amine functional unsaturated monomer is a dimethylaminoalkyl acrylate, a dialkylaminoalkyl methacrylate, a dialkylaminoalkoxy acrylate and/or a dialkyl-aminoalkoxy methacrylate.

6. (Amended) A process according to claim 1, wherein the tertiary amine functional unsaturated monomer is [preferably] dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, diethylaminoethyl acrylate, diethylaminoethyl methacrylate, or 2-(diethylamino) ethanol vinylether.

7. (Amended) A process according to claim 1, wherein the tertiary amine functional unsaturated monomer is present in a ratio to the anionic residues to be neutralized in the polyurethane prepolymer from between approximately 0.3 to 2.

8. (Amended) A process according to claim 1, wherein the anionic group in the polyurethane or in the polyurethane/polyacrylate hybrid is a carboxyl, a sulphonic, a sulphate and/or a phosphate group.

9. (Amended) A process according to claim 1, wherein the amount of carboxylic acid functions in the isocyanate functional polyurethane prepolymer is from approximately 1 to 15%.

10. (Amended) A process according to claim 2 wherein the hydroxy functional unsaturated monomer is a hydroxy functional acrylate or methacrylate selected from the group consisting of hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxy-propyl acrylate, hydroxypropyl methacrylate, hydroxybutyl acrylate, hydroxybutyl methacrylate, and hydroxy-polyester acrylate or methacrylate.

11. (Amended) A process according to claim 1, wherein the other vinylic monomers are selected from acrylic or methacrylic alkyl esters.

12. (Amended) A process according to claim 11, wherein the other vinylic monomers are present in an amount of approximately 0 to 90%.

13. (Amended) A process according to claim 1, wherein the polyurethane and/or the acrylic monomers contain additional functional groups selected from the group consisting of polyalkoxy functions with a large concentration of ethoxy functions, tertiary amine or quaternary amine functions, perfluor functions, incorporated silicon functions, hydrazide functions or hydrazone functions, ketone, acetoacetate, hydroxy, methylol, amide, glycidyl, and ureido or aldehyde functions.

14. (Amended) A process according to claim 1, wherein a conventional non-ionic, anionic or cationic surfactant is applied during the dispersion of the prepolymer solution in water.

15. (Amended) A dispersion prepared by the process of claim 1.

16. (Amended) A coating or film obtained from a dispersion prepared by the process of claim 1.

**REMARKS**


This preliminary amendment is being offered to better elucidate Applicants' invention in American claim format without adding new matter. Entry of this amendment by the Examiner is respectfully requested. Attached hereto is a marked-up version of the changes made to the claims by the current amendment. The attached paper is captioned "Version with Markings to Show Changes Made."

Authorization is given to charge payment of any additional fees required, or credit any overpayment, to Deposit Acct. 13-4213.

Respectfully submitted,

Dated: 29 May 2001

By:

  
\_\_\_\_\_  
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**Version with Markings to Show Changes Made**

1. (Amended) A process for the preparation of an aqueous dispersion of an anionic polyurethane in which initially a tertiary aminofunctional acrylic monomer of formula I:



wherein

$\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  are organic groups which have no reactivity towards the double bond or the tertiary amine function,

is used as neutralizing agent for pendant carboxylic acid groups in dispersions of a polyurethane or a polyurethane-polyacrylate, whereafter the unsaturated monomers undergo in situ an addition

[polymerisation] polymerization, [optionally together with other unsaturated monomers,]

[characterized in that] wherein the aqueous dispersion of the anionic polyurethane is prepared by the steps of

- [-] preparing [preparation of] an isocyanate functional anionic polyurethane prepolymer, optionally in the presence of vinylic monomers
- [-] mixing [of] the isocyanate terminated anionic polyurethane prepolymer with a tertiary-amino functional unsaturated monomer and optionally other vinylic monomers
- [-] followed by dispersing [dispersion] of the obtained mixture into water, and chain extension of the polyurethane prepolymer with an active hydrogen compound during or after the dispersion in water,
- [-] initiating radical [polymerisation] polymerization of the vinylic monomers, including the tertiary amino functional unsaturated monomers.

2. (Amended) A process according to claim 1, in which the isocyanate terminated prepolymer is reacted with 0-100% of a stoichiometric amount of a hydroxy functional unsaturated monomer before the dispersion of water.

3. (Amended) A process according to claim 1 [or 2], in which the tertiary amine functional acrylic oligomer or polymer is formed during the process by radical [polymerisation] polymerization of tertiary amine functional unsaturated monomers.

4. (Amended) A process according to claim 1 [to 3], in which the tertiary amine functional unsaturated monomers react together with other vinylic monomers during the radical [polymerisation] polymerization to obtain a tertiary amine functional co-polymer.

5. (Amended) A process according to claim 1 [any of the preceding claims], wherein the tertiary amine functional unsaturated monomer is a dimethylaminoalkyl acrylate, a dialkylaminoalkyl methacrylate, a dialkylaminoalkoxy acrylate and/or a dialkyl-aminoalkoxy methacrylate.

6. (Amended) A process according to claim 1 [any of the preceding claims], wherein the tertiary amine functional unsaturated monomer is [preferably] dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, diethylaminoethyl acrylate, diethylaminoethyl methacrylate, or 2-(diethylamino) ethanol vinylether [and the like].

7. (Amended) A process according to claim 1 [any of the preceding claims], wherein the tertiary amine functional unsaturated monomer is present in a ratio to the anionic residues to be neutralized in the polyurethane prepolymer from between approximately 0.3 to 2 [and preferably from 0.7 to 1.5].

8. (Amended) A process according to claim 1 [any of the preceding claims], wherein the anionic group in the polyurethane or in the polyurethane/polyacrylate hybrid is a carboxyl, a sulphonic, a sulphate and/or a phosphate group[and is preferably a carboxyl group].

9. (Amended) A process according to claim 1 [any of the preceding claims], wherein the amount of carboxylic acid functions in the isocyanate functional polyurethane prepolymer is from approximately 1 to 15% [and preferably from 2 to 10%].

10. (Amended) A process according to claim 2 [and any further preceding claim] wherein the hydroxy functional unsaturated monomer is a hydroxy functional acrylate or methacrylate [such as] selected from the group consisting of hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxy-propyl acrylate, hydroxypropyl methacrylate, hydroxybutyl acrylate, hydroxybutyl methacrylate, and hydroxy-polyester acrylate or methacrylate.

11. (Amended) A process according to claim 1 [any of the preceding claims], wherein the other vinylic monomers are selected from acrylic or methacrylic alkyl esters[, optionally functionalized with hydroxy, quaternary amines or halogen groups, acrylo-nitrile, styrene, esters and ethers of vinyl alcohol].

12. (Amended) A process according to claim 11 [and any of the preceding claims], wherein the other vinylic monomers are present in an amount of approximately 0 to 90% [and preferably from 0 to 60%].

13. (Amended) A process according to claim 1 [any of the preceding claims], wherein the polyurethane and/or the acrylic monomers contain additional functional groups [which may be selected from the group consisting of polyalkoxy functions with a large concentration of ethoxy functions, [may be] tertiary amine or quaternary amine functions, perfluor functions, incorporated silicon functions, hydrazide functions or hydrazone functions, ketone, acetoacetate, hydroxy, methylol, amide, glycidyl, and ureido or aldehyde functions.

14. (Amended) A process according to claim 1 [any of the preceding claims], wherein a conventional non-ionic, anionic or cationic surfactant[s] is applied during the dispersion of the prepolymer solution in water[, which is preferably a compound based on a long-chain dialkyl sodium sulfo-succinate, arylalkyl-polyethoxyalkyl derivatives, highly ethoxylated polyurethane derivative and the like].

15. (Amended) A dispersion [Dispersions] prepared by [a] the process [described in] of claim 1 [the preceding claims].

16. (Amended) A coating or film obtained from a dispersion prepared by [a] the process of claim 1 [as claimed in any of the claims 1 to 15].

Process for the preparation of anionic aqueous polymer  
dispersions containing no volatile tertiary amine,  
obtained dispersion and coating resulting from said  
dispersion

The present invention relates to a process to  
prepare aqueous dispersions of anionic polyurethanes and  
polyurethane-polyacrylate hybrids containing tertiary  
amino functional acrylic oligomers, polymers or copolymers  
5 as acid-neutralizing agents, in the absence of volatile  
tertiary amines.

### Introduction

Aqueous dispersions of polyurethanes or polyure-  
thane-polyacrylate hybrids are well known as basis for the  
10 production of coating compositions. They may be used for  
protective or decorative coating, optionally in combina-  
tion with additives like coloring agents, pigments,  
matting agents, and the like. Polyurethanes can posses  
15 many desirable properties such as good chemical  
resistance, water resistance, solvent resistance,  
toughness, abrasion resistance, durability. Thermoplastic  
polyurethane-polyacrylate hybrid dispersions became of  
interest regarding to polyurethanes because of their lower  
20 raw material costs and they became of interest regarding  
to polyacrylates because of their better performance

As is by now well known in the art, aqueous  
polyurethane dispersions are particularly advantageously  
prepared by dispersing an isocyanate-terminated  
25 polyurethane prepolymer bearing ionic and/or non-ionic  
dispersing groups into an aqueous medium and than reacting  
the prepolymer with an active hydrogen containing chain  
extender while dispersed in the aqueous medium. See e.g.  
UK-patents 1549458 and 1549459.

30 Generally polyurethane-polyacrylate hybrids are  
prepared by an addition polymerisation of acrylic monomers  
in a polyurethane dispersion. The acrylic monomers can be  
added to the polyurethane dispersion, which is described

in for example DE 1953348, EP643734 but they can also be added during the preparation of the polyurethane dispersion at several stages, which is described in for example US 4644030, EP742239. The vinylic monomers can be added during or after the polyurethane prepolymer formation and in these cases they function as viscosity reducing solvents. The advantage is that no or less other organic solvents have to be used, and a better homogeneity is obtained. The addition polymerisation is executed after the formation of the aqueous polyurethane. Moreover, further vinylic monomers may be added during the polymerisation as described in for example EP 308115.

Dispersibility of the polyurethanes or polyurethane-polyacrylate hybrids in water can be achieved by incorporation of appropriate chain pendant ionic groups, chain pendant non-ionic hydrophilic groups, or in-chain non-ionic hydrophilic groups in the structure of the polyurethane polymer. If suitable, external surfactants can be applied in addition. Preferably anionic groups are incorporated into the polyurethane backbone, such as carboxylic, sulfonic, sulfate or phosphate groups, by reaction of an isocyanate reactive compound having at least one acid group with a polyisocyanate. Most common is the incorporation of a carboxylic acid functional compound.

The carboxylic acid functions are generally neutralized before or during dispersion of the polyurethane prepolymer or prepolymer-vinylic monomer solution in water with a volatile tertiary amine. Anorganic bases are less convenient, since the polyurethane will coagulate when they are applied or it will provide highly water sensitive films or coatings. To prevent coagulation it is suitable to incorporate a great number of hydrophilic polyethoxy chains into the polymer system.

A disadvantage of the application of volatile tertiary amines as neutralizing agent is that they

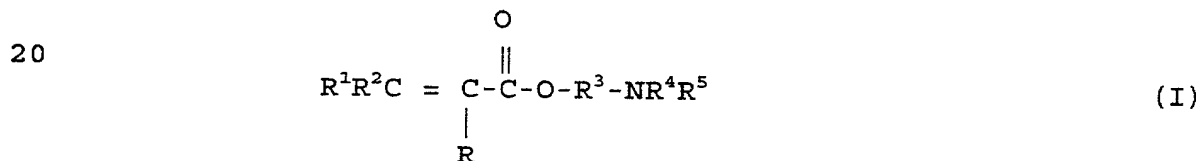
evaporate during the film formation, and therefore will cause environmental pollution.

The present invention offers a process to prepare aqueous dispersions of anionic polyurethanes or of  
 5 polyurethane-polyacrylate hybrids containing no volatile tertiary amines.

### Description of the invention

The object of the present invention is to provide  
 10 a process to prepare a dispersion of a polyurethane or a polyurethane-polyacrylate hybride which contains no volatile tertiary amines as neutralizing agents for carboxylic acid groups.

Accordingly the present invention relates to a  
 15 process for the preparation of an aqueous dispersion of an anionic polyurethane in which initially a tertiary amino-functional acrylic monomer of formula I



wherein,  
 25 R, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> are organic groups which have no reactivity towards the double bond or the tertiary amine function, is used as neutralizing agent for pendant carboxylic acid groups in dispersions of a polyurethane or a polyurethane/polyacrylate, whereafter  
 30 the unsaturated monomers undergo in situ an addition polymerisation, optionally together with other unsaturated monomers,

characterized in that the aqueous dispersion of the anionic polyurethane is prepared by the steps of  
 35 - preparation of an isocyanate functional anionic polyurethane prepolymer, optionally in the presence of vinylic monomers

- 4 -

- mixing of the isocyanate terminated anionic polyurethane prepolymer with a tertiary-amino functional unsaturated monomer and optionally other vinylic monomers
- 5 - followed by dispersion of the obtained mixture into water, and chain extension of the polyurethane prepolymer with an active hydrogen compound during or after the dispersion in water,
- initiating radical polymerisation of the vinylic  
10 monomers, including the tertiary amino functional unsaturated monomers.

Advantage of this process is that after the polymerisation of the unsaturated monomers containing a tertiary amine the dispersions contain no volatile amines  
15 and therefore environmental problems will be eliminated. Another advantage of the process is that the unsaturated monomers containing a tertiary amine function act as viscosity reducing solvents during the formation of the aqueous polyurethane. This effect is improved when other  
20 unsaturated monomers are present as well and an aqueous dispersion of a polyurethane-polyacrylate hybride is formed. In both situations less or sometimes even no other organic solvents have to be used, and a better homogeneity is obtained.

25 A further part of the invention is a process in which the isocyanate terminated prepolymer is reacted with 0-100% of a stoichiometric amount of a hydroxy functional unsaturated monomer before the dispersion in water.

As a result the polyurethane prepolymer is  
30 completely or partially functionalized with acrylic double bonds by complete or partial reaction of the isocyanate functions of the prepolymer with a hydroxy functional unsaturated monomer. As a result the polyurethane polymer system will contain double bonds and will contribute to  
35 the addition polymerisation.

The acid groups in the prepolymer are initial-ly neutralized by a tertiary amine functional unsaturated

monomer. In the process of the invention a tertiary amine functional acrylic polymer is formed during the process by radical polymerisation of the tertiary-amino functional unsaturated monomers. When other unsaturated monomers are present a copolymer will be formed during the process including the tertiary amine functional unsaturated monomers and the other unsaturated monomers. The other vinylic monomers which may be present are selected from acrylic alkyl esters, methacrylic alkyl esters, styrene, esters or ethers of vinyl alcohol. The other vinylic monomers are present in an amount of 0 to 90 %.

The present invention further comprises the dispersions prepared by the process and coatings or films derived from dispersions prepared by the process.

At low levels of other vinylic monomers or, without the presence of vinylic monomers, the performance of the films or coatings of the dispersions will be comparable with the performance of the films or coatings of polyurethane dispersions. At higher levels of other vinylic monomers the performance of the films or coatings of the dispersions will be comparable with the performance of the films or coatings of polyurethane-polyacrylate hybride dispersions.

Both the polyurethane and the acrylic monomers may contain additional functional groups with the objective to improve the waterdispersibility, to improve adhesion to substrates at application, for performance reasons, or as potential sites for crosslinking. Suitable functions are polyalkoxy functions with a large concentration of ethoxy functions, are tertiary amine or quaternary amine functions, perfluor functions, incorporated silicon functions, hydrazide functions or hydrazone functions, ketone, acetoacetate, hydroxy, methylol, amide, glycidyl, ureido or aldehyde functions.

### Detailed description of the invention

The tertiary amine functional unsaturated monomer which is used in the process of the invention can be a dialkylaminoalkyl acrylate, a dialkylaminoalkyl methacrylate, a dialkyl aminoalkoxy acrylate and/or a dialkylaminoalkoxy methacrylate. Suitable examples are dimethylaminoethyl acrylate, dimethyl-aminoethyl methacrylate, diethylaminoethyl acrylate, diethyl-aminoethyl methacrylate, 2-(diethylamino)ethanol vinyl ether and the like.

The tertiary amine functional unsaturated monomers are present in a ratio to the anionic residues to be neutralized in the polyurethane prepolymer from 0.3 to 2 and preferably from 0.7 to 1.5

When the isocyanate functional polyurethane prepolymer is reacted with a hydroxy functional unsaturated monomer the reaction is carried out by techniques well known in the art at 40 to 130°C. The hydroxy functional unsaturated monomer may be hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, hydroxybutyl acrylate, hydroxy butyl methacrylate, hydroxypolyester acrylates or methacrylates.

The polyurethane and/or polyurethane-polyacrylate hybriide contains anionic groups to obtain water dispersibility. This anionic group can be a carboxyl, a sulfonic, a sulfate and/or a phosphate group and is preferably a carboxyl group.

The isocyanate functional polyurethane prepolymer containing carboxylic acid groups is prepared in a conventional way. EP 308115 presents an overview of the process and of suitable polyols and polyisocyanates as starting materials for such polyurethane prepolymers. Ketone functional polyester polyols are included as well. Suitable hydrogen reactive chain extenders and the conditions wherein they are used are described in the same application.

The amount of carboxylic acid functions in the isocyanate functional polyurethane prepolymer is from 1 to 15 % and preferably from 2 to 10 %. The carboxylic acid functions are introduced in the prepolymer by incorporation of a dihydroxy alkanolic acid, which may be a 2,2-dimethylol alkanolic acid and is preferably 2,2-dimethylol propanoic acid.

In order to obtain polyurethane-polyacrylate hybrids, other vinylic monomers may be added. They can be added completely or partially to the polyurethane prepolymer or, preferably the polyurethane prepolymer is formed in the presence of the vinylic monomers. By combining the polyurethane prepolymer with the vinylic monomers an optimal homogeneity is obtained and the viscosity will be reduced. As a consequence less additional solvents will be needed. The vinylic monomers can be further added completely or partially after dispersion of the polyurethane prepolymer in water, during or after the chain extension. They further can be partially added during the radical polymerisation process.

Suitable vinylic monomers which can be used in addition are selected from acrylic or methacrylic alkyl esters, acrylic or methacrylic alkyl esters, optionally functionalized with hydroxy, quaternary amines or halogen groups, acrylonitrile, styrene, esters and ethers of vinyl alcohol.

The final proportion of additional vinylic monomers may vary from 0 up to 90 %, and preferably from 0 to 60 %.

The tertiary amine functional unsaturated monomer may be mixed with the polyurethane prepolymer, optionally in the presence of other vinylic monomers and be dispersed in water using techniques well known in the art. Preferably, water is stirred into the mixture with agitation or, alternatively, the mixture is added to the water and optionally the chain extender with agitation. Alternatively the polyurethane prepolymer, optionally in

the presence of other vinylic monomers is added to a mixture of water and the tertiary amine functional unsaturated monomer and optionally the chain extender with agitation.

5           Regularly the ratio of tertiary amine functions to the acid groups in the polyurethane prepolymer is from 0.3 to 2 and preferably from 0.7 to 1.5. At lower levels of the tertiary amine functional acrylate, the final dispersion will have a lower pH value, which may be  
10   advantageous for some crosslinking applications.

Polymerisation of the tertiary amine functional unsaturated compound or combination of the tertiary amine functional unsaturated compound and other vinylic monomers may be effected by the methods described in EP308115.

15           The polyurethane and/or the acrylic monomers of the invention may contain additional functional groups which may be polyalkoxy functions with a large concentration of ethoxy functions, may be tertiary amine or quaternary amine functions, perfluor functions,  
20   incorporated silicon functions, hydrazide functions or hydrazone functions, ketone, aceto-acetate, hydroxy, methylol, amide, glycidyl, ureido or aldehyde functions.

Conventional non-ionic, anionic or cationic surfactants may be applied to optimize dispersion of the  
25   polymer system in water and stabilisation of the final polymer dispersion. Suitable examples may be based on long-chain dialkyl sodium sulphosuccinate, arylalkylpolyethoxyalkyl derivatives, highly ethoxylated polyurethane derivatives and the like.

30           The aqueous polymer dispersions produced by the method of the invention are stable for long periods of time. If desired minor amounts of solvents may be included in the dispersions.

Many additional ingredients may also be present  
35   in the application stage, for example fillers, colorants, pigments, silicones, flow agents, foam agents, fire retardants and the like.

The aqueous polymer dispersions produced by the method of the invention may be used in adhesives, sealants, printing ink and in coatings. They may be applied on any substrates, including leather or artificial leather, metals, wood, glass, plastics, paper, paper board, textile, non-woven, cloth, foam and the like by conventional methods, including spraying, flow-coating, roller-coating, brushing, dipping, spreading and the like.

Various aspects of the present invention are illustrated by the following examples. These examples are only illustrative and are not limiting the invention as claimed hereafter.

### Examples

#### Example 1

Preparation of an aqueous polyurethane dispersion containing a copolymerized tertiary amine functional methacrylate.

26.33 g (118.5 mmole) of 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate (hereafter referred to as IPDI) was added to a mixture of 53.2 g (26.6 mmole) of a polycarbonate diol with a molecular weight of about 2000 (obtainable from Stahl USA as PC-1122) and 5.28 g (37.45 mmole) of 2,2-dimethylol-propanoic acid in 12 g of N-methylpyrrolidone at 60°C while mixing. The mixture was heated to 90°C and the mixture was reacted at 90°C for 2 hrs. After 1 hr of reaction time 0.01 g of tinocatoate was added as a catalyst. The reaction mixture was cooled down. The amount of NCO in the obtained prepolymer was 4.32%.

2.43 g (15.46 mmole) of dimethylaminoethyl methacrylate (hereafter referred to as DMAEMA) was mixed with 39.27 gram of the the prepolymer at 55 °C for 20 min. The neutralized prepolymer was dispersed into 57.28 g of demineralized water and the polyurethane prepolymer was chain extended by the addition of 0.96 g (19.2 mmole) of

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hydrazine hydrate. The mixture was stirred for 30 min. The absence of residual NCO was checked by IR-spectroscopy.

12 g of butyl acrylate and 22.3 g of water were mixed in the polyurethane and the tertiary amine functional methacrylic monomer was polymerized together with the butyl acrylate within one hour at 75-80°C, using 0.03 g of t-butylhydroperoxide and 1.01 g of a 1% solution in water of isoascorbic acid as redox initiation system. The obtained product had a solids amount of 34 % and a pH of 6.9.

#### Example 2

Preparation of an aqueous polyurethane dispersion containing a copolymerized tertiary amine functional methacrylate.

The process for the preparation of the polyurethane dispersion of example 1 was repeated up to and including the extension with hydrazine. 2.43 g of butyl acrylate, 2 g of dioctyl sodium sulphosuccinate and 10 g of water were added to the polyurethane dispersion and the tertiary amine functional methacrylic monomer was polymerized together with the butyl acrylate within one hour at 75-80°C, using 0.03 g of t-butylhydroperoxide and 1.01 g of a 1% solution in water of isoascorbic acid as redox initiation system. The obtained product was adjusted with water to a solids amount of 35 % and it had a pH of 6.9.

#### Example 3

Preparation of an aqueous polyurethane dispersion containing a copolymerized tertiary amine functional methacrylate.

The process of example 2 was repeated with the exception that the polyurethane prepolymer was prepared from 22.89 g (103 mmole) of IPDI, 60.00 g (30 mmole) of polycarbonate diol and 3.6 g (25.53 mmole) of 2,2-dimethylolpropanoic acid in 10 g of N-methylpyrrolidone

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and the NCO-amount of the obtained prepolymer was 3.58%. Further, 1.66 g (10.56 mmole) of DMAEMA was mixed with 38.4 g of the prepolymer and 59.08 g of water was used for the dispersion. The obtained polyurethane dispersion was mixed with 1.63 g of butyl methacrylate and 2 g of dioctyl sodium sulphosuccinate, whereafter the tertiary amine functional methacrylic monomer was polymerized together with the butyl methacrylate within one hour at 75-80°C, using 0.03 g of t-butylhydroperoxide and 1.01 g of a 1% solution in water of isoascorbic acid as redox initiation system. The obtained product was adjusted with water to a solids amount of 35 % and it had a pH of 7.

#### Example 4

Preparation of an aqueous polyurethane dispersion containing a copolymerized tertiary amine functional methacrylate.

The process of example 2 was repeated with the exception that the DMAEMA was replaced by 2.86 g of diethyl-aminoethyl methacrylate.

#### Example 5

Preparation of a hydrazon functional chain extender 100 g (1 mole) of ethylacrylate was added within 45 min to 170 g (1 mole) of isophoron diamine at 40-45 C. The mixture was stirred for 4 hrs at 40-45°C. The reaction was checked by the disappearance of the double bond signals at 960 and 1600  $\text{cm}^{-1}$  in the infrared spectrum. The intermediate product was a ethyl N-aminopropionate functional isophorone diamine. 50 g of hydrazine hydrate (1 mole) was added to the product at 55°C and the product was heated and stirred at 55-60°C during 5 hrs. The reaction was checked by the disappearance of the carbonyl signal at 1740  $\text{cm}^{-1}$  from the ester carbonyl and de appearance of the carbonyl signal from the hydrazide carbonyl at 1650  $\text{cm}^{-1}$  in the infrared spectrum. The second intermediate product was a N-hydrazido-propionate

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functional isophorone diamine. 58 g (1 mole) of acetone was added to the obtained product at ambient temperature and the mixture was stirred for 15 min. The product was a isophorone diamine substituted at one N by an 3-propionyl  
5 hydrazone. The product contained 2.65 meq/g of hydrazone functions and 5.29 meq/g of amine functions.

#### Example 6

Preparation of an hydrazone functional aqueous  
10 polyurethane dispersion containing a copolymerized tertiary amine functional methacrylate.

The process of example 5 was repeated with the exception that the hydrazine was replaced by a mixture of 7.26 g of the product of example 5 and 7.26 g of water.  
15 The obtained product had a solids amount of 35.4%, a hydrazone functionality of 0.145 meq/g and a pH of 7.9.

#### Example 7

Preparation of an aqueous polyurethane dispersion  
20 containing a copolymerized tertiary amine functional methacrylate.

33.27 g (149.7 mmole) of IPDI was added to a mixture of 45.4 g (22.7 mmole) of a polytetramethylene glycol with a molecular weight of about 2000 (obtainable as Terathane 2000 from Du Pont de Nemours) and 6 g (27.0  
25 mmole) of 2,2-dimethylol-propanoic acid in 12 g of N-methylpyrrolidone at 60°C while mixing. The mixture was heated to 90° and the mixture was reacted at 90°C for 2 hrs. After 1 hr of reaction time 0.01 g of tinocatoate was  
30 added as a catalyst. The reaction mixture was cooled down. The amount of NCO in the obtained prepolymer was 7.00%.

1.67 Gram (11.7 mmole) of dimethylaminoethyl acrylate and 8 g of butylacrylate were mixed with 26.10 gram of the prepolymer at 55°C for 20 min. The neutralized  
35 prepolymer was dispersed into 71.30 g of demineralized water and the polyurethane prepolymer was chain extended by the addition of 1.03 g (20.6 mmole) of hydrazine

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hydrate. The mixture was stirred for 30 min. The absence of residual NCO was checked by IR-spectroscopy.

8.34 g of butyl acrylate was added to 69.52 g of the polyurethane dispersion and the tertiary amine functional methacrylic monomer and the butyl acrylate monomer were polymerised within one hour at 75-80°C, using t-butyl-hydroperoxide and isoascorbic acid as redox initiation system. The obtained product had a solids amount of 34.0 % and a pH of 7.0.

#### Example 8

Preparation of an aqueous polyurethane dispersion containing a copolymerized tertiary amine functional methacrylate.

The process of example 7 was repeated with the exception that the butylacrylate which was mixed with the polyurethane prepolymer and the dimethylaminoethyl acrylate was replaced by ethylhexylacrylate.

The product was adjusted to a solids amount of 35 % with water and the pH was 7.2.

#### Example 9

Preparation of an aqueous polyurethane dispersion containing a copolymer of a tertiary amine functional methacrylate, butylacrylate and an acetoacetyl functional methacrylate. The process of example 2 was repeated with the exception that before the initiation of the addition polymerisation the butylacrylate was replaced by 1 g of acetoacetoxyethyl methacrylate, 10 g of butylacrylate and 18 g of water was added to the dispersion and the DMAEMA was polymerised together with the acetoacetoxyethyl methacrylate and the butyl acrylate. The obtained product had a solids amount of 35.2 %, a pH of 7.1 and an acetoacetate functionality of 0.215 meq/g.

#### Example 10

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Preparation of an aqueous dispersion of a polyurethane containing pendant ketone functions and containing a copolymer of a tertiary amine functional methacrylate and butylacrylate.

5 Under a nitrogen atmosphere 182.33 g (0.13 mole) of a polyester diol with a OH number of 80 and containing ketone functions (available from NeoResins as PEC-205), 12.06 g (0.09 mole) of dimethylol-propanoic acid and 94.4 g of N-methylpyrrolidone were heated to 70°C while  
10 stirring. 88.8 g (0.4 mole) of IPDI was added and the mixture was heated to 100°C and stirred for 2 hrs to form a polyurethane prepolymer. After 1 hr of reaction time 0.04 g of tinocatoate was added as catalyst. The reaction was cooled down and the amount of remaining NCO appeared  
15 to be 2.87%.

110 g of the polyurethane prepolymer was mixed with 4.28 g of DMAEMA and 4 g of dioctyl sodium sulpho-succinate and the mixture was dispersed into 120 g of water. 1.79 g of hydrazine hydrate in 4.2 g of water was  
20 added within 5 min and the dispersion was stirred for 30 min. The NCO-signal in the IR-spectrum at 2240 cm<sup>-1</sup> was disappeared.

4.28 g of butyl acrylate was added and polymerisation of the DMAEMA together with the butyl  
25 acrylate was effected within one hour at 75-80°C. The obtained product was adjusted with water to a solids amount of 35.0 % and had a pH of 7.0.

## Example 11

Preparation of an aqueous polyurethane dispersion which is copolymerized with a tertiary amine functional methacrylate and with butyl methacrylate.

5           24.14 g (108.6 mmole) of IPDI was added to a mixture of 53.2 g (26.6 mmole) of the polycarbonate diol of example 1, 1.5 g (3.57 mmole) of a polypropylene glycol diol with a molecular weight of 420 and 3.52 g (25 mmole) of 2,2-dimethylol-propanoic acid in 12 g of N-methyl-  
10 pyrrolidone at 60°C while mixing. The mixture was heated to 90° and the mixture was reacted at 90°C for 2 hrs. After 1 hr of reaction time 0.01 g of tinocatoate was added as a catalyst.

          The reaction mixture was cooled down. The amount  
15 of NCO in the obtained prepolymer was 4.40%.

          0.006 Gram of inhibitor MEHQ (methylether of hydroquinone) was added to 94.07 gram of the prepolymer at 75°C. After stirring for ten minutes, 5.92 g (51 mmole) of 2-hydroxyethylacrylate was added. The reaction mixture was  
20 stirred for 3 hours at 75-80°C and then cooled down to 55°C. The resulting intermediate prepolymer was partially capped with the hydroxy ethylacrylate and had a NCO-amount of 1.79%.

          The prepolymer was neutralised by mixing 1.49  
25 gram of DMAEMA with 37.05 gram of the intermediate prepolymer at 55°C for 20 min. 1.88 gram of dioctyl sodium-sulfosuccinate was mixed with 1.88 gram of N-methyl-pyrrolidone and added to the prepolymer mix. The neutralized prepolymer mix was dispersed in demineralised  
30 water for 45 minutes and the polyurethane prepolymer was chain extended with hydrazine. The absence of residual NCO was checked by IR-spectroscopy.

          2 gram of dioctyl sodium sulphosuccinate and 1.35 gram of butyl methacrylate were added to 88.3 gram of the  
35 polyurethane dispersion. The tertiary amine functional acrylic monomer together with the double bonds of the polyurethane and of the butyl methacrylate was polymerised

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at 75°C using 0.05 gram of t-butylhydroperoxide and 1.5 gram of a 1% iso-ascorbic acid solution in water. A post-treatment of 1 hour was made with the same portions of initiators.

- 5           The obtained dispersion had a solids amount of 36.4 % and a pH of 7.2

#### Comparative examples 12-15

- 10           Preparation of polyurethane dispersions in which triethylamine is the neutralization agent for carboxylic acid groups.

- 15           The process of example 2, 3, 6, and 7 were repeated with the exception that the DMAEMA was replaced by a stoichiometric amount of triethylamine, and the products were adjusted to a solids amount of 35 %. Triethylamine is a conventional neutralizing agent for the carboxylic acid functions in the polyurethane. The comparative examples 12, 13, 14, and 15 correspond with respectively the examples 2, 3, 6, and 7.

- 20           Example 16

          This example is concerned with the evaluation of the films of the products of example 2, 3, 6, 7, 12, 13, 14, and 15.

- 25           Films of 200 and 600  $\mu\text{m}$  were prepared of the products of example 2, 3, 6, 7 and of the corresponding comparative examples 12, 13, 14, and 15. Further films were prepared of the products of example 6 and 14 together with XR-5350, is a NCO-crosslinker obtainable from Stahl  
30           Holland. The mechanical properties of the films were determined. Further the weight increase of the films in water was measured after treatment of the films with water for 24 hours. The results are presented in tabel 1. The results show that the film properties of the polyurethanes  
35           from which the carboxylic acid functions were neutralized with DMAEMA, whereafter the DMAEMA was polymerised by addition polymerisation, were comparable with those from

which the carboxylic acid functions were neutralized by triethylamine. They had comparable mechanical properties and the sensitivity towards water was just slightly less, but had no consequences in application onto leather.

- 5 During the drying process the polymerized DMAEMA stayed in the film, while the triethylamine was evaporated.

Table 1

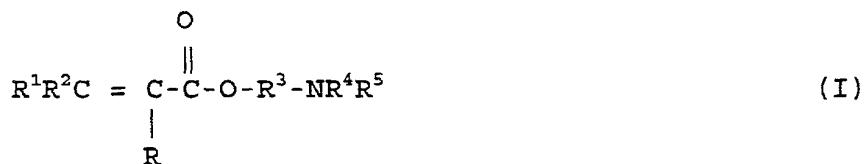
Film of example	Mechanical properties (MPa) <sup>a)</sup>				weight increase of the films in water
	M-100	M-200	M-300	Elongation	(%)
3	4.5	6.4	11.0	370	14
4	3.5	5.1	7.5	420	12
6	5.3	7.8	13.2	340	13
6 + XR-5350	15.4	22.6	--	250	4
7	3.9	6.0	9.6	360	15
12	4.4	6.3	10.7	360	17
13	3.6	5.2	7.6	460	15
14	5.5	7.9	13.6	320	15
14 + XR-5350	15.7	23.0	--	240	6
15	4.0	6.2	9.9	350	19

notes to table 1:

- a) MPa is megapascal ( $10^6 \text{ Nm}^{-2}$ ). The mechanical properties and the elongation are measured with films which were stretched at a thickness of 200  $\mu\text{m}$  on a MTS Synergie 200 apparatus. The values at M-100, M-200, M-300 give tensile strenghts of the films while stretching them for respectively 50, 100, 150, 200, 300 %. The elongation is the maximal elongation before the film breaks.

CLAIMS

1. A process for the preparation of an aqueous dispersion of an anionic polyurethane in which initially a tertiary aminofunctional acrylic monomer of formula I



wherein,

R, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> are organic groups which have no reactivity towards the double bond or the tertiary amine function,

is used as neutralizing agent for pendant carboxylic acid groups in dispersions of a polyurethane or a polyurethane/polyacrylate, whereafter the unsaturated monomers undergo in situ an addition polymerisation, optionally together with other unsaturated monomers,

characterized in that the aqueous dispersion of the anionic polyurethane is prepared by the steps of

- preparation of an isocyanate functional anionic polyurethane prepolymer, optionally in the presence of vinylic monomers
- mixing of the isocyanate terminated anionic polyurethane prepolymer with a tertiary-amino functional unsaturated monomer and optionally other vinylic monomers
- followed by dispersion of the obtained mixture into water, and chain extension of the polyurethane prepolymer with an active hydrogen compound during or after the dispersion in water,
- initiating radical polymerisation of the vinylic monomers, including the tertiary amino functional unsaturated monomers.

2. A process according to claim 1, in which the isocyanate terminated prepolymer is reacted with 0-100% of a stoichiometric amount of a hydroxy functional unsaturated monomer before the dispersion in water.

5           3. A process according to claim 1 or 2, in which the tertiary amine functional acrylic oligomer or polymer is formed during the process by radical polymerisation of tertiary amine functional unsaturated monomers.

10           4. A process according to claim 1 to 3, in which the tertiary amine functional unsaturated monomers react together with other vinylic monomers during the radical polymerisation to obtain a tertiary amine functional copolymer.

15           5. A process according to any of the preceding claims, wherein the tertiary amine functional unsaturated monomer is a dialkylaminoalkyl acrylate, a dialkylaminoalkyl methacrylate, a dialkylaminoalkoxy acrylate and/or a dialkyl-aminoalkoxy methacrylate.

20           6. A process according to any of the preceding claims, wherein the tertiary amine functional unsaturated monomer is preferably dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, diethylaminoethyl acrylate, diethylaminoethyl methacrylate, 2-(diethylamino)ethanol vinylether and the like.

25           7. A process according to any of the preceding claims, wherein the tertiary amine functional unsaturated monomer is present in a ratio to the anionic residues to be neutralized in the polyurethane prepolymer from 0.3 to 2 and preferably from 0.7 to 1.5.

30           8. A process according to any of the preceding claims, wherein the anionic group in the polyurethane or in the polyurethane/polyacrylate hybrid is a carboxyl, a sulphonic, a sulphate and/or a phosphate group and is preferably a carboxyl group.

35           9. A process according to any of the preceding claims, wherein the amount of carboxylic acid functions in

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the isocyanate functional polyurethane prepolymer is from 1 to 15% and preferably from 2 to 10%.

10. A process according to claim 2 and any further preceding claim wherein the hydroxy functional unsaturated monomer is a hydroxy functional acrylate or methacrylate such as hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxy-propyl acrylate, hydroxypropyl methacrylate, hydroxybutyl acrylate, hydroxybutyl methacrylate, a hydroxy-polyester acrylate or methacrylate.

11. A process according to any of the preceding claims, wherein the other vinylic monomers are selected from acrylic or methacrylic alkyl esters, optionally functionalized with hydroxy, quaternary amines or halogen groups, acrylo-nitrile, styrene, esters and ethers of vinyl alcohol.

12. A process according to claim 11 and any of the preceding claims, wherein the other vinylic monomers are present in an amount of 0 to 90% and preferably from 0 to 60%.

13. A process according to any of the preceding claims, wherein the polyurethane and/or the acrylic monomers contain additional functional groups which may be polyalkoxy functions with a large concentration of ethoxy functions, may be tertiary amine or quaternary amine functions, perfluor functions, incorporated silicon functions, hydrazide functions or hydrazone functions, ketone, acetoacetate, hydroxy, methylol, amide, glycidyl, ureido or aldehyde functions.

14. A process according to any of the preceding claims, wherein a conventional non-ionic, anionic or cationic surfactants is applied during the dispersion of the prepolymer solution in water, which is preferably a compound based on a long-chain dialkyl sodium sulpho-succinate, arylalkyl-polyethoxyalkyl derivatives, highly ethoxylated polyurethane derivatives and the like.

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15. Dispersions prepared by a process described in the preceding claims.

16. A coating or film obtained from a dispersion prepared by a process as claimed in any of the claims 1 to

5 15.

Docket No.  
30394-1045

US 90272 WO 14/60

# Declaration and Power of Attorney For Patent Application

## English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

**PROCESS FOR THE PREPARATION OF ANIONIC AQUEOUS POLYMER DISPERSIONS  
CONTAINING NO VOLATILE TERTIARY AMINE, OBTAINED DISPERSION AND COATING  
RESULTING FROM SAID DISPERSION**

the specification of which

(check one)

☐ is attached hereto.

☒ was filed on May 29 2001 and Oct 16 2000 as United States Application No. or PCT International Application Number USSN 09/ 857,006 and PCT/NL00/00740, respectively and was amended on \_\_\_\_\_

(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d) or Section 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)

Priority Not Claimed

<u>PCT/NL00/00740</u>	<u>PCT</u>	<u>16 October 2000</u>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	
<u>NL 101330</u>	<u>Netherlands</u>	<u>15 October 1999</u>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	
_____	_____	_____	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	

I hereby claim the benefit under 35 U.S.C. Section 119(e) of any United States provisional application(s) listed below:

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

I hereby claim the benefit under 35 U. S. C. Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. Section 112, I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, C. F. R., Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Status)  
(patented, pending, abandoned)

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Status)  
(patented, pending, abandoned)

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Status)  
(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. *(list name and registration number)*

**Jeffrey D. Myers, Reg. No. 35,964**

Send Correspondence to:

**CUSTOMER NO. 005179**




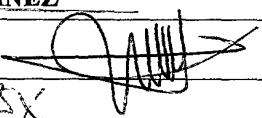
**05179**

PATENT TRADEMARK OFFICE

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ESX

[illegible]

Table 1	
Year	Age
1990	1990
1991	1991
1992	1992
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1995	1995
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